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(54) **NOUVEAU SOLVANT ET COMPOSITION ELECTROLYTIQUE
A HAUTE CONDUCTIVITÉ AYANT UNE STABILITÉ A
LARGE PLAGE**

(54) **NEW SOLVENT AND ELECTROLYTIC COMPOSITION WITH
HIGH CONDUCTIVITY AND WIDE STABILITY RANGE**

New Solvent and Electrolytic Composition with high Conductivity and Wide Stability Range

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Field of invention:

Aprotic solvents useful as media for organic reactions and/or synthesis; ionically conductive material obtained when a salt is added as a solute; solid or gel polymer electrolytes resulting from the incorporation of said solvent with a salt to a polymer; liquid or solid electrolyte useful for electrochemical applications, like lithium batteries or so-called rocking chair or lithium-ion batteries, by extension to other metallic ions (mono, di and trivalent) or non metallic (ammonium); electrochromic devices as for window, large screen displays or optical devices, supercapacitors

Background of invention:

US patents 4,851,307 and 5,063,124 claim a new ionically conductive materials which comprise a salt dissolved in a solvent or a mixture in variable amounts of this solvent with an polymer bearing solvating groups; said solvent being a sulfamide derivative of general formula :

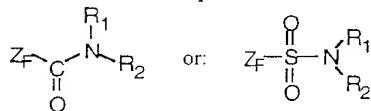


wherein R_1 , R_2 , R_3 and R_4 are each independently a C(1-10) alkyl group or a C(1-10) oxaalkyl group. A representative example of this group is $R_1 = R_2 = R_3 = R_4 =$ ethyl.

US patent (xxxx) to Penwalt Corporation claims dielectric insulating media of the perfluoro acylamides or sulfonamides $R_F S O_2 N A_1 A_2$ and $R_F S O_2 N A_1 A_2$, where A_1 and A_2 are alkyl groups.

Brief description of the invention:

In opposition the claims of (xxx), it was found in the present invention that molecules of the type:



R_1 , R_2 , being each independently a C(1-10) alkyl group or a C(1-10) oxaalkyl group, an alkylene or an oxaalkylene group.

Z_F being either F, R_F , a C(1-10) essentially perhalogenated alkyl-, oxa-alky or aza alkyl group, an $R_F C H_2 O^-$ group, an $(R_F C H_2)_2 N^-$ groups,

Are not dielectric insulators and present high conductivities when ionic solutes are present. Salts of low lattice energies which are easily soluble in such liquids include metallic salts of delocalized anions, I^- , CIO_4^- , BF_4^- , PF_6^- , AsF_6^- , SbF_6^- , $R_F SO_3^-$, $XSO_2NSO_2X^-$, $(XSO_2)(X' SO_2)X^-$, X , X' and X'' being independently chosen among: Z_F , R, with at least one X being either Z_F , 4,5-dicyano-1,2,3-triazole, 3,5-bis(R)-1,2,4-triazole, tricyano methane, pentacyanocyclopentadiene, pentakis(trifluo-

5 (methyl)cyclopentadiene anions salts, $Z_FSO_2NCN^-$, $Z_FSO_2C(CN)_2^-$. Similarly, ionic salt may include ammonium, pyridinium, amidinium, imidazolium, phosphonium, sulfonium, substituted or not by alkyl-, oxa-alkyl or aza-alkyl, aryl, alkylaryl or arylalkyl groups. By essentially perhalogenated it is meant that the degree of halogenation on the chain fluorination on the chain is sufficient to provide properties similar to those of a perhalogenated chains. Preferably, at least 3 quarters of hydrogen atoms are replaced by fluorine, possibly complemented by chlorine atoms.

In addition to the unexpected finding of solvating properties of such material, it has been found that the resulting solutions have an outstandingly wide electrochemical stability range, extending from 0 to ≥ 3.8 0 V vs. Li^+/Li° , which renders accessible the electrochemistry of high valency transition metal derivative without parasitic reactions. Electrochemical devices using the the object of the invention are thus safe to operate, which is not the case with conventional organic solvents when poised at highly positive or negative potentials.

5 Example 1:

0 Trifluoromethanesulfonic anhydride in dichloromethane is added at $0^\circ C$ to an excess of 40% dimethylamine solution in water. After completion of the addition. The organic layer is separated, washed with acidified water, dried with anhydrous magnesium sulfate. The corresponding amide $CF_3SO_2N(CH_3)_2$ has a dielectric constant of 40, a sharp melting point of $-40^\circ C$ as measured by DSC and viscosity of xx cP.

Example 2:

5 Trifluoromethanesulfonic anhydride (5g, 17.7 mmol) in 10mL dichloromethane is added at $0^\circ C$ to 2.1 g of N-methyl-ethylamine in 10mL dichloromethane. The organic layer is separated, washed with acidified water, dried with anhydrous magnesium sulfate. The corresponding amide $CF_3SO_2N(CH_3)C_2H_5$ has a dielectric constant of 37, can be quenched to a glass (transition temperature $T_g = -xx$) and viscosity of xx cP.

Example 3:

0 Trifluoroethanol (18.2 mL, 25 mmol) in 100mL of ether are added to 7 g of sodium hydride. After the gas evolution has ceased, the solution is centrifuged and the supernatant clear liquid is added at $0^\circ C$ to 35 g (25 mmol) of dimethylsulfamoyl chloride in 100 mL of dry ether under stirring. A white precipitate of NaCl forms and the reaction is completed in two hours. The slurry is filtered and the ether stripped in a rotary evaporator. The residue is diluted with 50 ml of dichloromethane and washed with water. The organic layer is separated, dried with anhydrous magnesium sulfate. The corresponding trifluoroethyl-N,N-dimethylsulfamate is distilled under reduced pressure.

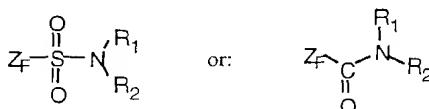
Example 4:

5 300 mg of lithium bis(trifluoromethane sulfonimide) (LiTFSI) are dissolved into 1 mL of the amide of example 1. The resulting solution has a

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What is claimed is:

1) a ion conducting liquid or solid composition containing amides of general formula:



used alone or in admixtures, characterized in that R_1 , R_2 , being each independently a C(1 - 10) alkyl group or a C(1-10) oxaalkyl group, an alkylene or an oxaalkylene group.

5 Z_F being either F, R_F , a C(1 - 10) essentially perhalogenated alkyl-, oxa-alky or aza alkyl group, an $\text{R}_F\text{CH}_2\text{O}$ - group, an $(\text{R}_F\text{CH}_2)_2\text{N}^-$ groups.

10 2) ion conducting liquid or solid composition according to claim 1 characterized in that the halogen is fluorine.

3) ion conducting liquid or solid composition according to claim 1 and 2 characterized in that the halogen a low lattice energy salt is dissolved at least partly within.

4) ion conducting liquid or solid composition according to claim 1 and 2 characterized in that low lattice 5 energy salt is contains a metal cation with an anion chosen among I^- , ClO_4^- , BF_4^- , PF_6^- , AsF_6^- , SbF_6^- , R_FSO_3^- , $\text{XSO}_2\text{NSO}_2\text{X}'^-$, $(\text{XSO}_2)(\text{X}'\text{SO}_2)(\text{X}''\text{SO}_2)\text{C}^-$, X , X' and X'' being independantly chosen among: Z_F , R, with at least one X being either Z_F , 4,5-dicyano-1,2,3-triazole, 3,5-bis(R)1,2,4-triazole, tricyano methane, pentacyanocyclopentadiene, pentakis(trifluoromethyl)-cyclopentadiene anions salts, $\text{Z}_F\text{SO}_2\text{NCN}^-$, $\text{Z}_F\text{SO}_2\text{C}(\text{CN})_2^-$, or mixture thereof.

0 5) ion conducting liquid or solid composition according to claim 1 and 2 characterized in that low lattice 5 energy salt is contains a cation chosen among ammonium, pyridinium, amidinium, imidazolium, phoshonium, sulfonium, substituted or not by alkyl-, oxa-alkyl or aza-alkyl , aryl, alkylaryl or arylalkyl groups.

6) electrolytic composition according to claims 1 to 5 characterized in that the amides are used alone or in admixture with a co-solvent or an aprotic polymer or both.

7) electrolytic composition according to claims 1 to 6 characterized in that one of the salt is a lithium salt.

8) electrolytic composition according to claims 1 to 7 characterized in that the co-solvent is chosen among the dialkyl ethers of ethylene glycol, diethylene glycol, triethylene glycol, and/or ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, γ -butyrolactone.

9) electrolytic composition according to claims 7 and 10 characterized in that the polymer is chosen among polyethers comprising at least 70 % ethylene oxide units, poly(methyl methacrylate), poly(acrylonitrile)polymethacrylonitrile, copolymers containing at least 70% vinylidene fluoride units.

10) electrolytic composition according to claims 1 to 9 and characterized in that the amount of solvent to polymer ratio is less than or equal to 20% and acts as a plasticizer.

11) electrolytic composition according to claims 1 to 9 and characterized in that the amount of solvent to polymer ratio is greater or equal to 50% and the resulting mixture constitutes a gel.

5 12) lithium battery characterized in that the electrolyte, alone or as a component of the composite electrodes is chosen among electrolytic compositions according to claims 1 to 11.

10 13) lithium battery according to claims 14 characterized in that the negative electrode contains either metallic lithium, a lithium alloy, a carbon intercalation compound or a low voltage intercalation oxide or nitride.

15 14) lithium battery according to claims 14 and 15 characterized in that the positive electrode contains a high voltage intercalation electrode derived from vanadium, manganese, cobalt or nickel oxides, lithium iron or manganese phosphate or pyrophosphate,

20 15) lithium battery according to claims 14 and 15 characterized in that the positive electrode contains a polydisulfide or sulfur mixed with a conductive additive like high surface area carbon.

25 16) super capacity according characterized in that the electrolyte is made according to claims 1 to 11

20 17) super capacity according to claim 16 characterized in that the the electrode materials are high surface-area carbon

18) super capacity according to claim 16 characterized in that the the negative electrode material is chosen among metallic lithium, a lithium alloy, a carbon intercalation compound or a low voltage intercalation oxide or nitride and the positive electrode contains a high voltage intercalation electrode derived from vanadium, manganese, cobalt or nickel oxides, lithium iron or manganese phosphate or pyrophosphate,

25 19) super capacity according to claim 16 characterized in that the the negative electrode contains is a "n" dopable polymer and the positive electrode contains is a "p" dopable polymer.